



101 102004/00 7860

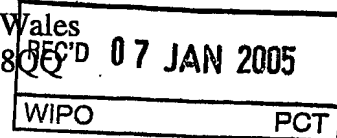


INVESTOR IN PEOPLE

PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH
RULE 17.1(a) OR (b)

The Patent Office
Concept House
Cardiff Road
Newport

South Wales
NP10 806

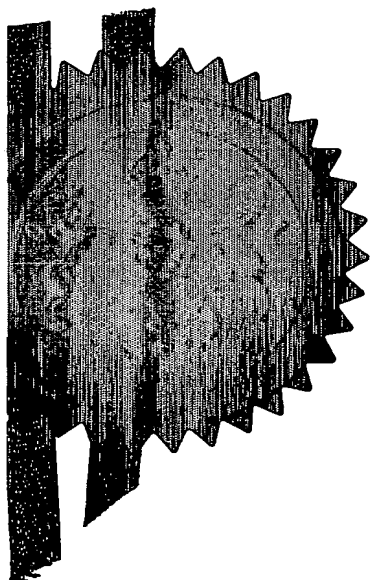


I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

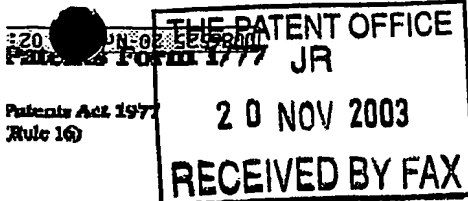
Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.



Signed *William Morell*

Dated 10 December 2004

BEST AVAILABLE COPY



Patents Act 1977
Rule 16)

Request for grant of a patent
(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office
Cardiff Road
Newport
Gwent NP9 1RH

1. Your reference	SMC 60630/GB/P		
2. Patent application number (The Patent Office will fill in this part)	0326997.4		20 NOV 2003
3. Full name, address and postcode of the or of each applicant (underline all surnames)	Avecia Limited Hexagon House Blackley Manchester, M9 8ZS United Kingdom 07764137001 GB		
Patents ADP number (if you know it)			
If the applicant is a corporate body, give the country/state of its incorporation	GB		
4. Title of the invention	COMPOUNDS		
5. Name of your agent (if you have one)	MAYALL, John		
"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)	Avecia Limited Hexagon House Blackley Manchester, M9 8ZS United Kingdom		
Patents ADP number (if you know it)	8244313002	6244313004	
If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number	Country	Priority application number (if you know it)	Date of filing (day / month / year)
If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application	Date of filing (day / month / year)	
Is a statement of inventors and of right to grant of a patent required in support of this request? (Answer 'Yes' if: a) any applicant named in part 3 is not an inventor, or b) there is an inventor who is not named as an applicant, or c) any named applicant is a corporate body. See note (4))			

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form

Description

17

Claim(s)

02

Abstract

Drawing(s)

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventors' right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

1 cover sheet

11.

I/we request the grant of a patent on the basis of this application.

Signature

C. Shepherd

Date 20/11/03

Avecia Limited Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

Mrs K.M. Pinder/Mrs G. Shepherd 0161 721 1361/2

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered "Yes" Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

COMPOUNDS

This invention relates to compounds suitable for use as dyes, to inks and to their use in ink jet printing ("IJP"). IJP is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

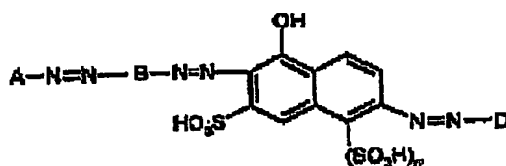
There are many demanding performance requirements for dyes and inks used in IJP. For example they desirably provide sharp, non-feathered images having good water-fastness, ozone-fastness, light-fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink jet nozzle because this will stop the printer from working. The inks should also be stable to storage over time without decomposing or forming a precipitate which could block the fine nozzle.

JP10195320 describes dyes including tris-azo dyes carrying a pyrazolyl azo group and their use in the coloration of paper and pulp.

US patent application 2001/0027734 describes metal complexes of tris-azo dyes derived from tris-azo molecules optionally containing a (substituted) pyrazolylazo moiety. The copper complexes are said to be particularly preferred.

We have surprisingly found that certain non-metallised compounds provide valuable colorants for ink jet printing inks.

According to the present invention there is provided a compound of Formula (1) or salt thereof:



Formula (1)

wherein:

A is optionally substituted phenyl or naphthyl;

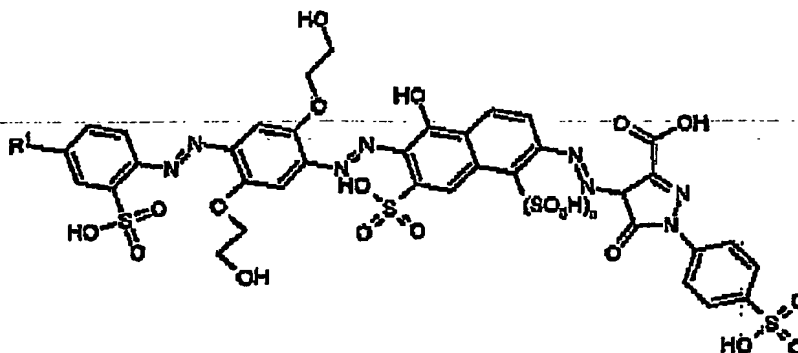
B is optionally substituted phenylene or naphthylene;

n is 0 or 1;

D is a pyrazolyl group; and

wherein the compound of Formula (1) is not of Formula (2) or a salt thereof;

2



Formula (2)

wherein:

R^1 is C_{1-4} alkyl or C_{1-4} alkoxy; and

n is 0 or 1.

Preferably A is optionally substituted phenyl.

Preferably B is optionally substituted phenylene. The optional substituents which may be present on A or B are preferably selected from hydroxy, halo, nitro, cyano, carboxy, sulphy, phosphato, optionally substituted amino (especially amino or amino carrying one or more C_{1-4} alkyl groups), optionally substituted acylamino (especially C_{1-4} acylamino or phenylacylamino, each of which optionally carries a sulphy or a carboxy group), optionally substituted ureido (especially ureido or ureido carrying one or two C_{1-4} alkyl groups), optionally substituted C_{1-6} alkyl, optionally substituted C_{1-6} alkoxy, optionally substituted C_{1-6} alkylthio, optionally substituted aryl, optionally substituted C_{1-4} alkyl sulphonyl and optionally substituted sulphonamido (especially sulphonamido or sulphonamido carrying one or two C_{1-4} alkyl groups). Preferably A carries at least one water-solubilising group selected from carboxy, sulphy and phosphato.

As examples of optionally substituted phenyl and naphthyl groups represented by A there may be mentioned 4-amino-2,5-disulphophenyl, 2-sulpho-4-methoxyphenyl, 2-carboxy-4-sulphophenyl, 2-sulpho-4-methyl and 2-sulpho-4,5-dimethylphenyl.

In one aspect of the present invention there is provided a compound of Formula (1) with the proviso that when A is optionally substituted phenyl, A is free from nitro groups.

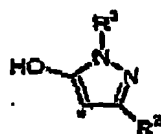
The optional substituents on B are preferably selected from carboxy, sulphy, phosphato, optionally substituted amino, acylamino, optionally substituted ureido, optionally substituted alkyl, optionally substituted alkoxy and optionally substituted aryl.

When B is substituted phenylene it preferably carries one or more groups selected from optionally substituted C_{1-6} alkyl, optionally substituted C_{1-6} alkylthio, optionally substituted C_{1-6} alkoxy, optionally substituted amino, optionally substituted ureido, carboxy

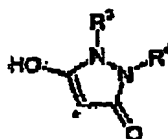
and sulphato. When B is optionally substituted naphthylene the naphthylene ring preferably carries one or more water solubilising groups, more preferably by one or two groups selected from carboxylic, sulphonic and phosphonic acid groups.

As examples of optionally substituted phenylene and naphthylene groups represented by B there may be mentioned 2,5-di(2-hydroxyethoxy)phen-1,4-yleno, 2,5-dimethoxyphen-1,4-yleno, 2,5-diethoxyphen-1,4-yleno, 2-methoxy-5-aminophen-1,4-yleno, 2-methoxy-5-acetylaminophen-1,4-yleno.

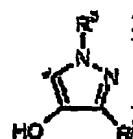
Preferably D is a pyrazolyl group carrying at least one carboxy, sulpho or phosphato group. In an especially preferred embodiment, D is a pyrazoloryl group of Formula (3a), (3b) or (3c):



Formula (3a)



Formula (3b)



Formula (3c)

wherein

R² and R³ are each independently H, carboxy, cyano or optionally substituted alkyl, alkoxy, acyl, aryl, amino, amido, carbonamido, carboxyester, sulphonamoyl or alkylsulphonyl; and

R³ and R⁴ are each independently H or optionally substituted aryl or alkyl;

where the asterisk * shows the point of attachment to the azo linkage in Formula (1).

R² is preferably an optionally substituted C₁₋₆-alkyl, C₁₋₆-acyl or amino group or a group capable of hydrogen bonding in the free acid form with the adjacent azo group such as carboxy. More preferably R² is carboxy.

Preferred optionally substituted C₁₋₆-alkyl groups are optionally substituted C₁₋₄-alkyl, more preferably C₁₋₄-alkyl which is unsubstituted or carries a halo atom or a carboxy, sulpho or phosphato group.

Preferred optionally substituted C₁₋₆-alkoxy groups are optionally substituted C₁₋₄-alkyl, more preferably C₁₋₄-alkyl which is unsubstituted or carries a halo atom or a carboxy, sulpho or phosphato group.

Preferred optionally substituted phenyl groups are those mentioned above for A.

Preferred optionally substituted sulphonamide groups are of the formula

SO₂NR⁶R⁷ wherein R⁶ and R⁷ are each independently H, optionally substituted C₁₋₆ alkyl.

Preferred optionally substituted amino groups are optionally substituted acylamino, especially C₁₋₄-acylamino, more preferably optionally substituted ureido which is unsubstituted or carries a carboxy, sulpho or phosphato group.

Preferably acyl groups are optionally substituted C₁₋₄alkylacyl, optionally substituted phenylacyl, preferably acetyl or benzoyl.

Preferred substituents which may be present on the optionally substituted C₁₋₄alkyl, C₁₋₄alkoxy, C₁₋₈alkylthio, aryl (especially phenyl), C₁₋₈alkylsulphonyl substituents on any of A, B, R², R³, R⁴, R⁵, R⁶ and R⁷ are selected from hydroxy, halo, nitro, cyano, carboxy, sulphy, phosphato, acylamino, ureido, C₁₋₈alkyl, C₁₋₄alkoxy, C₁₋₁₀alkylthio, aryl, C₁₋₈alkyl sulphonyl and sulphonamido.

As examples of groups represented by R² there may be mentioned methyl, carboxy and H.

R³ and R⁴ are preferably each independently an optionally substituted aryl group, more preferably phenyl or naphthyl carrying one or two substituents selected from carboxy or sulphy.

As examples of groups represented by R³ and R⁴ there may be mentioned 4-sulphophenyl and 2-sulphonaphthyl.

R⁵ is preferably carboxy or a C₁₋₄alkylcarboxyester.

In view of the above preferences, in a preferred embodiment:

A is phenyl carrying one or two substituents selected from carboxy, sulphy, phosphato, amino, methyl, methoxy and acetamido;

B is phenylene or naphthylene carrying one or two substituents selected from sulphy, methyl, methoxy and 2-hydroxyethoxy;

n is 0 or 1;

D is of Formula (3a), (3b) or (3c);

R² is H, methyl or carboxy;

R³ and R⁴ are each independently phenyl or naphthyl carrying one or two substituents selected from sulphy and carboxy; and

R⁵ is a C₁₋₄alkylcarboxyester.

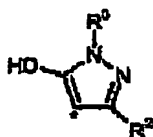
In a further preferred embodiment:

A is phenyl carrying one or two substituents selected from carboxy, sulphy, amino, methyl, methoxy and acetamido.

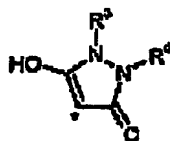
B is phenylene or naphthylene carrying one or two substituents selected from sulphy, methyl and methoxy 2-hydroxyethoxy.

n is 0 or 1;

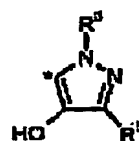
D is of Formula (3a), (3b) or (3c):



Formula (3a)



Formula (3b)



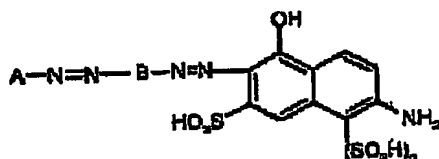
Formula (3c);

R^2 and R^5 are each independently H, carboxy, cyano or optionally substituted alkyl, alkoxy, acyl, aryl, amino, amido, carbonamido, carboxyester, sulphamoyl or alkylsulphonyl; and

R^3 and R^4 are each independently H or optionally substituted aryl or alkyl;

5 where the asterisk * shows the point of attachment to the azo linkage in Formula (1).

The compounds of Formula (1) may be prepared by diazotising a compound of the Formula (4) wherein n, A and B are as hereinbefore defined to give a diazonium salt and coupling the resultant diazonium salt with a compound of Formula H-D wherein D is as hereinbefore defined:



Formula (4).

The diazotisation is preferably performed at a temperature of 0°C to 10°C . Preferably the diazotisation is performed in water, preferably at a pH below 7. Dilute mineral acid, e.g. HCl or H_2SO_4 , may be used to achieve the desired pH conditions.

15 The compound of Formula (4) may be prepared by diazotising a compound of Formula $\text{A}-\text{N}=\text{N}-\text{B}-\text{NH}_2$ to give a diazonium salt and coupling the resultant diazonium salt with 1-hydroxy-3-sulpho-6-aminonaphthylene optionally carrying a sulphonyl group at the 8-position; wherein A and B are as hereinbefore defined. Reaction conditions are those generally used in the dyestuff art, for example as described in for example EP 20 0366080.

25 When the compound of Formula (1) is in the form of a salt the preferred salts are alkali metal salts (especially lithium, sodium and potassium salts), ammonium and substituted ammonium salts and mixtures thereof. Especially preferred salts are sodium, potassium and lithium salts, salts with ammonia and volatile amines and mixtures thereof. The lithium salts have good solubility, forming particularly storage stable inks with low toxicity and no tendency to block ink jet nozzles.

30 The compounds may be converted into a desired salt using known techniques. For example, an alkali metal salt of a compound may be converted into the ammonium or substituted ammonia salt by dissolving an alkali metal salt of the compound in water, acidifying with a mineral acid and adjusting the pH of the solution to pH 9 to 9.5 with ammonia or the amine and removing the alkali metal cations by dialysis or by use of an ion exchange resin.

Examples of amines which may be used to form such salts include methylamine, dimethylamine, trimethylamine, ethylamine, n-propylamine, iso-propylamine, n-

butylamine, iso-butylamine, sec-butylamine, tert-butylamine, piperidine, pyridine, morpholine, allylamine, diethylamine, triethylamine, tetramethyl amine and mixtures thereof. It is not essential that the dyes are completely in the form of the ammonium salt or substituted ammonium salt and mixed alkali metal and either ammonium salt or substituted ammonium salt are effective; especially those in which at least 50% of the cations are ammonium or substituted ammonium ions.

Still further salts are those with the counter ions described in US 5830265, claim 1, integer (b), which are included herein by reference thereto.

The compounds of Formula (1) may exist in tautomeric forms other than those shown in this specification. These tautomers are included within the scope of the present claims.

In a second aspect of the present invention there is provided a composition which comprises a compound of Formula (1) as hereinbefore defined and a liquid medium, wherein the liquid medium comprises water and an organic solvent.

A preferred composition according to the second aspect comprises:

(a) from 0.01 to 30 parts of a compound of Formula (1) or salt thereof; and

(b) from 70 to 99.99 parts of a liquid medium;

wherein the liquid medium comprises an organic solvent and all parts are by weight and the number of parts of (a)+(b)=100.

The number of parts of component (a) is preferably from 0.1 to 20, more preferably from 0.6 to 15, and especially from 1 to 5 parts. The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts. Preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10%. This allows the preparation of liquid dye concentrates which may be used to prepare inks and reduces the chance of the dye precipitating if evaporation of the liquid medium occurs during storage.

Preferred liquid media comprise water and an organic solvent, preferably in a weight ratio of water to organic solvent of 99:1 to 1:99, more preferably 99:1 to 50:50 and especially 95:5 to 80:20.

It is preferred that the organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-miscible organic solvents include C₁₋₆-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol,

The viscosity of the composition at 25°C is preferably less than 50cP, more preferably less than 20 cP and especially less than 5cP.

When the compositions according to the second aspect of the invention are used as ink jet printing compositions, the composition preferably has a concentration of halide ions of less than 500 parts per million, more preferably less than 100 parts per million. It is especially preferred that the composition has less than 100, more preferably less than 50 parts per million of divalent and trivalent metals, wherein parts refer to parts by weight relative to the total weight of the composition. We have found that purifying the compositions to reduce the concentration of these undesirable ions reduces nozzle blockage in ink jet printing heads, particularly in thermal ink jet printers. A further aspect of the invention provides a process for printing an image on a substrate comprising applying thereto a composition according to the second aspect of the present invention to the substrate by means of an ink jet printer.

The ink jet printer preferably applies the composition to the substrate in the form of droplets which are ejected through a small orifice onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the composition in a reservoir by means of a resistor adjacent to the orifice, thereby causing the composition to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink jet printers the oscillation of a small crystal causes ejection of the composition from the orifice.

The substrate is preferably paper, plastic, a textile, metal or glass, more preferably a treated substrate such as a coated paper or coated plastic, especially coated paper.

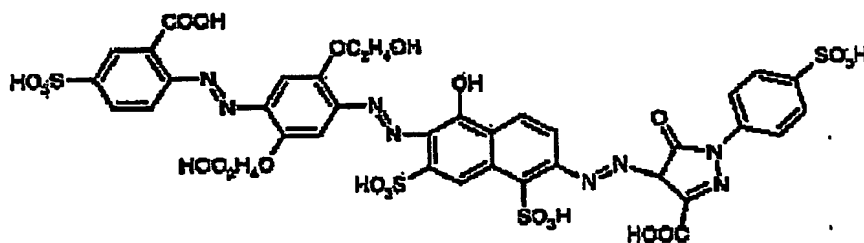
Preferred plain or treated papers are papers which may have an acid, alkaline or neutral character. Examples of commercially available treated papers include HP Premium Coated Paper, HP Photopaper (both available from Hewlett Packard Inc.); Stylus Pro 720 dpi Coated Paper, Epson Photo Quality Glossy Film, Epson Photo Quality Glossy Paper (all available from Seiko Epson Corp.); Canon HR 101 High Resolution Paper, Canon GP 201 Glossy Paper, Canon HG 101 and HG201 High Gloss Film and Canon PR101 (all available from Canon).

A further aspect of the present invention provides a paper, an overhead projector slide or a textile material printed with a composition, a compound or by means of a process as hereinbefore defined.

A still further aspect of the present invention provides an ink jet printer cartridge, optionally refillable, comprising one or more chambers and a composition, wherein the composition is present in at least one of the chambers and the composition is as defined in the second aspect of the present invention.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless specified otherwise.

Preparation of:



5-Sulphoanthranilic acid (44.4g, 32.55g@100%) was dissolved in water (500ml) by adjusting the pH to 8-9 with lithium hydroxide solution (2M) and sodium nitrite (11.4g) added. The solution was then added to a stirred mixture of ice & water containing concentrated hydrochloric acid (50ml). The reaction was further stirred for 1 hr at 0-10°C after which time excess nitrous acid was destroyed by addition of sulphamic acid.

A solution of 2,5-bis-(2-acetoxyethoxy)aniline (44.55g) in acetone (500ml) was added to the above prepared diazonium salt solution before stirring overnight allowing to self warm to room temperature. The product was isolated by filtration, washed with water, slurried in acetone (1.5litres) and again isolated by filtration before drying at 50°C. Yield = 82.5g.

The product from Stage A (28g) was suspended in N-methylpyrrolidone (250ml) and sodium nitrite (7.5g) added. After stirring for 10mins at room temperature a solution of concentrated hydrochloric acid (16ml) in water (100ml) was slowly added during which time the temperature rose to 45°C. The reaction mixture was stirred for 2hrs allowing to self-cool to room temperature and excess nitrous acid destroyed by the adding sulphamic acid.

6-Amino-1-naphthol-3,5-disulphonic acid (20g) was dissolved in water (200ml) by adjusting the pH to 8-9 with lithium hydroxide solution (2M). The above prepared diazonium salt solution was then slowly added at 0-10°C maintaining the pH at 7-8 by addition of lithium hydroxide solution (2M) as necessary. After stirring for 1hr lithium hydroxide (10g) was added and the reaction mixture stirred for a further 1hr at room temperature at which time thin layer chromatography showed the hydrolysis to be complete. The pH was adjusted to 7 by addition of concentrated hydrochloric acid and lithium chloride solution (50% w/v) added. After self cooling to room temperature the product was isolated by filtration and washed with lithium chloride solution (50% w/v). The product was purified by dissolving in water (200ml) and re-precipitating with acetone (2.5litres). The acetone was removed by decantation and the residue dissolved in water to give a solution that was found, by titration with titanous chloride, to contain 0.05 mole of product. The product was used in Stage C without further purification.

Stage C - Title Dye

The product from Stage B was stirred at room temperature and sodium nitrite (3.8g) and Calsolene™ oil (1g) added. The mixture was then added to a stirred mixture of ice & water containing concentrated hydrochloric acid (20ml). Stirring was continued for 2hrs at 0-10°C during which time the diazonium salt precipitated from solution as a suspension. A solution of 1-(4-sulphophenyl)-3-carboxypyrazol-5-one (15.5g) dissolved in water (200ml) and the pH adjusted to 7-8 by addition of lithium hydroxide solution (2M) was added to the diazonium salt suspension and stirring was continued for 1hr at 0-10°C maintaining the pH at 7-8 by addition of lithium hydroxide solution (2M) as necessary. The product was isolated by drown out into acetone (5litres) and subsequent filtration. The crude product was purified by dissolution in water (300ml) and repeating the drown out into acetone (2.5litres). After filtration the product was dissolved in water and dialysed to low conductivity and finally isolated by evaporation to dryness at 70°C. Yield = 46.3g.

Examples 2-9

The method of Example 1 was repeated except that in Stage A the 5-sulphoanthranilic acid was replaced with an amine of formula corresponding to the structure in column A of Table 1; where indicated by n=0, the 6-amino-1-naphthol-3,5-disulphonic acid was replaced with 6-Amino-1-naphthol-3-sulphonic acid; and in Example 9, Stage C, the 1-(4-sulphophenyl)-3-carboxypyrazol-5-one was replaced by the pyrazole of formula D as indicated in Table 1. The structure of the resultant compound is also shown in Table 1.

Table 1

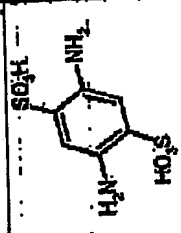
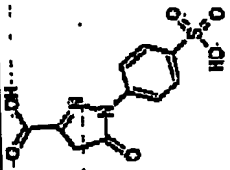
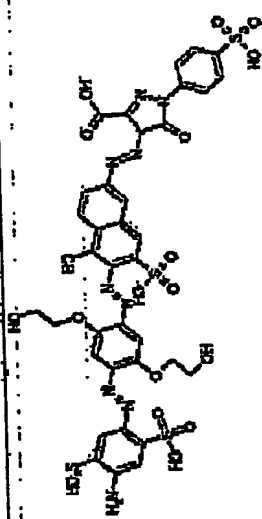
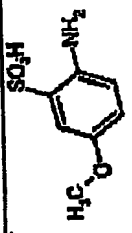
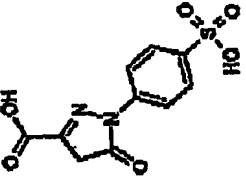
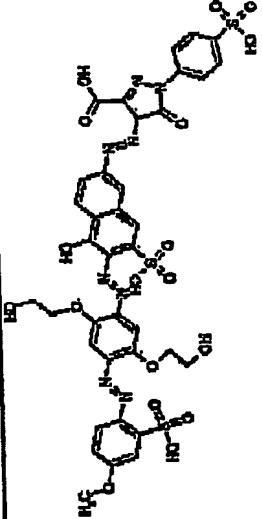
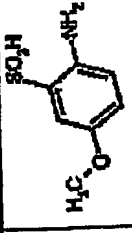
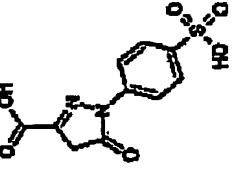
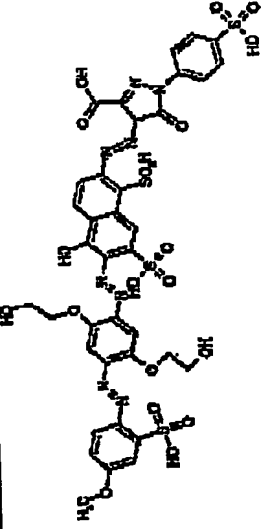
Exc	A	n	D	Final dye structure	λ_{max}/ϵ
2		0			604nm 70,200
3		0			594nm 54,200
4		1			588nm 66,100

Table 1 Continued

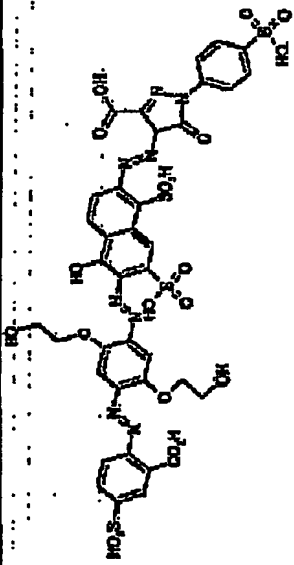
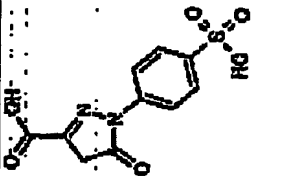
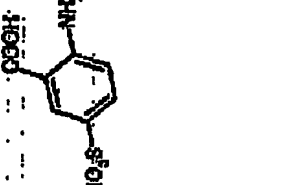
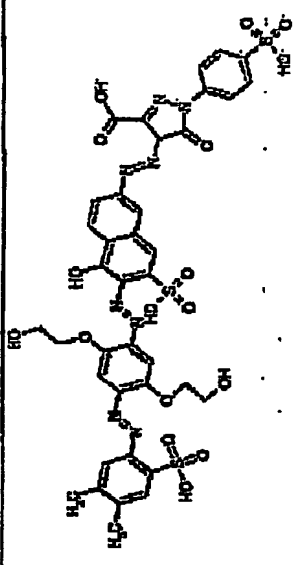
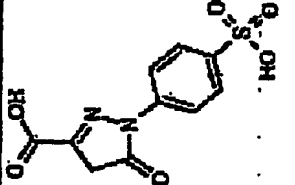
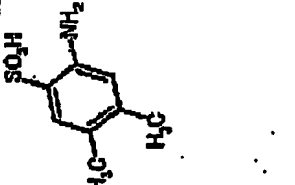
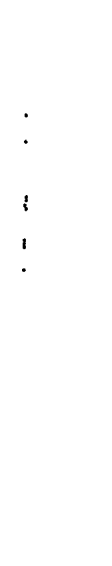
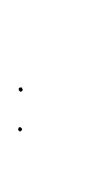

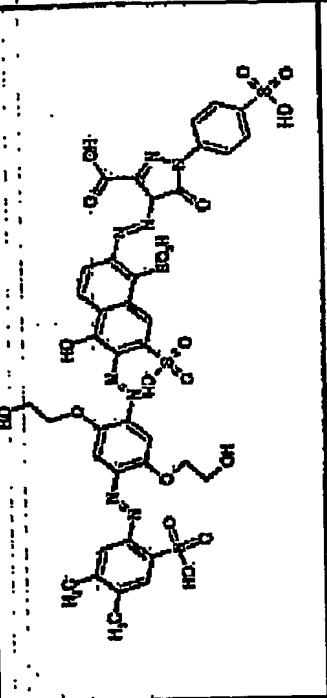
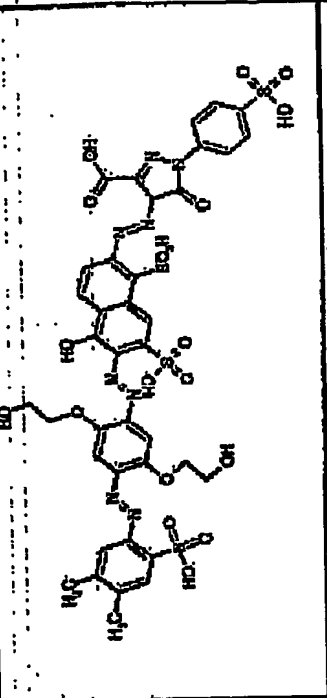
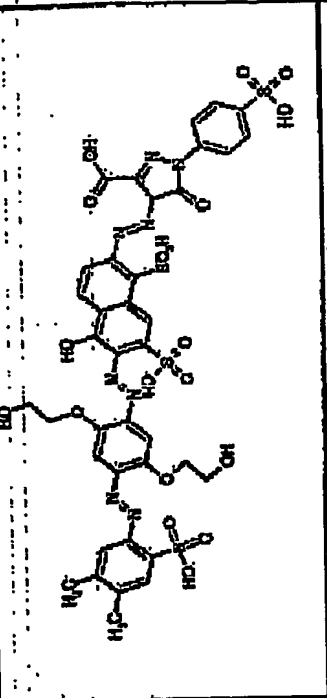

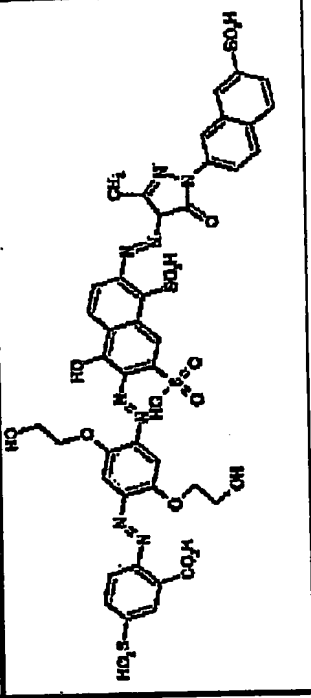
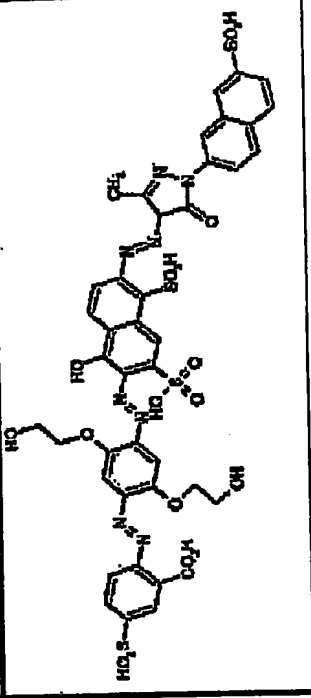
580nm 64,300			5
			
580nm 52,800			6
			
580nm 52,800			7
			

Table 1 Continued

581nm 63,300		604nm 55,700
		
		

Example 10 - Inks

Inks may be prepared containing the dyes from Example 1 to Example 9 according to the following formulation:

2-Pyrrolidone 5 parts
 Thiodiglycol 5 parts
 Surfynol™ 4651 part
 Dye 3 parts
 Water amount required to make up to 100 parts

Surfynol™ 465 is a surfactant available from Air Products and Chemicals Inc., USA.

Further inks may be prepared according to Tables 2 and 3 wherein the dye described in the first column is the dye made in the above example of the same number. Numbers quoted in the second column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo inkjet printing.

The following abbreviations are used in Tables 2 and 3:

PG = propylene glycol
 DEG = diethylene glycol
 NMP = N-methyl pyrrolidone
 DMK = dimethylketone
 IPA = isopropanol
 MECH = methanol
 2P = 2-pyrrolidone
 MIBK = methylisobutyl ketone
 P12 = propane-1,2-diol
 BDL = butane-2,3-diol
 CET = cetyl ammonium bromide
 PHO = Na₂HPO₄ and
 TBT = tertiary butanol
 TDG = thiodiglycol

Example 11 — Ink Jet Printing

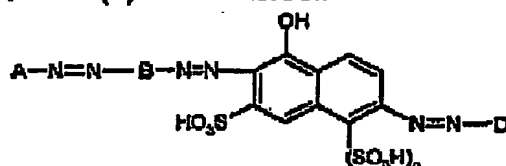
The inks prepared in Example 10 may be incorporated into an empty cartridge of a Hewlett Packard DeskJet 550C™ ink jet printer and printed onto e.g. Xerox X Acid™, Canon PR101 or Epson SEC PM paper to give prints of excellent optical density, shade, light and ozone fastness.

TABLE 2

Dye	Dye Content	Water	PG	DEG	NMP	DMK	NaOH	Na Stearate	IPA	MEOH	2P	MIBK
1	2.0	80	5		6	4					5	
2	3.0	90		5	5		0.2					
3	10.0	85	3		3	3				5	1	
4	2.1	91		8								1
5	3.1	88	5					0.2	4			5
6	1.1	81			9		0.5				9	
7	2.5	60	4	15	3	3			6	10	5	4
8	5	65		20					10			
9	2.4	75	5	4		5				6		5
10	4.1	80	3	5	2	10		0.3				
1	3.2	65		5	4	6			5	4	6	5
2	5.1	86								4		
3	10.8	90	5						5	4		
4	10.0	80	2	6	2	5			1		4	
5	1.8	80		5							15	
6	2.6	84			11						5	
7	3.3	80	2			10				2		6
8	12.0	90				7	0.3		3			
9	5.4	69	2	20	2	1					3	3
10	6.0	91			4						5	

CLAIMS

1. A compound of Formula (1) or salt thereof:



Formula (1)

wherein:

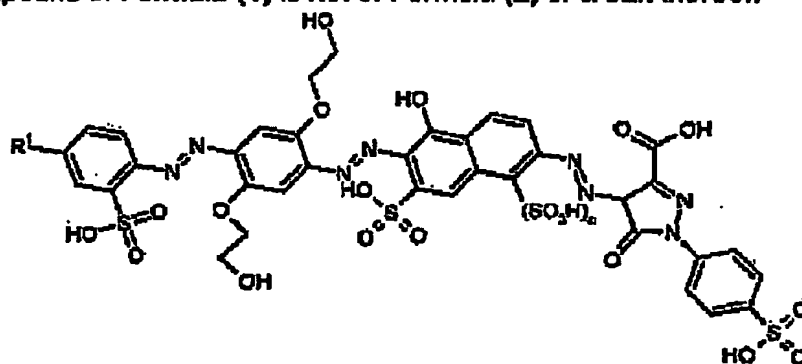
A is optionally substituted phenyl or naphthyl;

B is optionally substituted phenylene or naphthylene;

n is 0 or 1;

D is a pyrazolyl group; and

wherein the compound of Formula (1) is not of Formula (2) or a salt thereof;



Formula (2)

wherein:

R¹ is C₁₋₄ alkyl or C₁₋₄ alkoxy; and

n is 0 or 1.

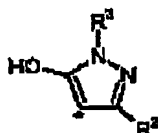
2. A compound according to claim 1 wherein D is a pyrazolyl group carrying at least one carboxy, sulpho or phosphonic acid group.

3. A compound according to any one of the preceding claims wherein:

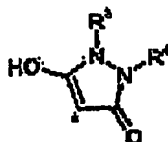
A is phenyl carrying one or two substituents selected from carboxy, sulpho, amino, methyl, methoxy and acetamido.

B is phenylene or naphthylene carrying one or two substituents selected from sulpho, methyl and methoxy 2-hydroxyethoxy.

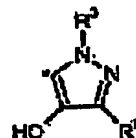
n is 0 or 1;
D is of Formula (3a), (3b) or (3c):



Formula (3a)



Formula (3b)



Formula (3c)

R² and R⁵ are each independently H, carboxy, cyano or optionally substituted alkyl, alkoxy, acyl, aryl, amino, amido, carbonamido, carboxyester, sulphonyl or alkylsulphonyl; and

R³ and R⁴ are each independently H or optionally substituted aryl or alkyl; where the asterisk * shows the point of attachment to the azo linkage in Formula (1).

4. A compound of Formula (1) as defined in claim 1, with the proviso that A is free from nitro groups when A is optionally substituted phenyl.

5. A compound according to any one of the Examples described herein.

6. A composition which comprises a compound of Formula (1) as defined in claim 1 and a liquid medium, wherein the liquid medium comprises water and an organic solvent.

7. A composition according to claim 6 which contains a further colorant selected from black, magenta, cyan or yellow colorants.

8. A process for printing an image on a substrate comprising applying thereto a composition according to any either of claims 6 or 7 by means of an ink jet printer.

9. A paper, an overhead projector slide or a textile material printed with a composition according to either of claims 6 or 7, a compound according to any one of claims 1 to 5, or by means of a process according to claim 8.

10. An ink jet printer cartridge, optionally refillable, comprising one or more chambers and a composition, wherein the composition is present in at least one of the chambers and the composition is according to either of claims 6 or 7.

PCT/GB2004/004868



**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☒ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.